



MINISTRY OF PRODUCTION ACTIVITIES

HEAD OFFICE FOR THE DEVELOPMENT OF INDUSTRY AND
COMPETITIVENESS

ITALIAN PATENT AND TRADEMARK OFFICE

PATENT FOR AN INDUSTRIAL INVENTION No.

01317261

The present patent is granted for the invention according to the
application as specified hereinbelow

Application nr.	Year	C.C.I.A.A. ¹	Application date	Classification
000850	2000	MILAN	14/04/2000	C08J

APPLICANT VALERIO FRANCESCHETTI ELASTOMERI S.P.A. WITH
SEAT IN CORTE FRANCA (BRESCIA)

REPRESENTATIVE RAPISARDI MARIACRISTINA

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TITLE PROCESS FOR MAKING A FOAMED THERMOPLASTIC
ELASTOMERIC MATERIAL, IN PARTICULAR FOR MAKING
CORKS OR CLOSURES FOR CONTAINERS IN
SUBSTITUTION OF NATURAL CORK, MATERIAL
OBTAINED THROUGH THIS PROCESS AND CLOSURES
MADE OF THIS MATERIAL

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ROME, 27 MAY 2003

THE DIRECTOR OF G7 OFFICE
ATTILIO RONCACCI

¹ Chamber of Commerce

GB B. A8600

TO THE MINISTRY OF COMMERCE AND HANDICRAFT

A FORM (STAMP)

ITALIAN PATENT AND TRADEMARK OFFICE (UIBM) - ROME

APPLICATION FOR A PATENT FOR AN INDUSTRIAL INVENTION. FILING OF
RESERVATIONS, PUBLIC AVAILABILITY IN ADVANCE

A. APPLICANT(S)

1) COMPANY NAME VALERIO FRANCESCHETTI ELASTOMERI S.P.A.
WITH SEAT IN NIGOLINE- CORTE FRANCA (BRESCIA)
FISCAL CODE 02127820170

2) COMPANY NAME -----
WITH SEAT IN -----

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C. ASSIGNEE DOMICILE OF CHOISE -----

IN ----- nr. -- CITY ----- postal code -----, prov. ---

D. TITLE Proposed class (sec./cl./subcl.)----- group/subgroup ---/-----
PROCESS FOR MAKING A FOAMED THERMOPLASTIC ELASTOMERIC MATERIAL, IN
PARTICULAR FOR MAKING CORKS OR CLOSURES FOR CONTAINERS IN
SUBSTITUTION OF NATURAL CORK, MATERIAL OBTAINED THROUGH THIS
PROCESS AND CLOSURES MADE OF THIS MATERIAL

PUBLIC AVAILABILITY IN ADVANCE YES NO X IF REQD. DATE --/--/-- FILE. NR.

E. DESIGNATED INVENTORS

	SURNAME	NAME		SURNAME	NAME
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2)	ROSSI	Simone	4)	-----	-----

F. PRIORITY

STATE OR ORGANIZATION	PRIORITY TYPE	APPL. NR.	FILING DATE	ATTACHMENT S/R	RESERVATIONS PUT ASIDE
1) -----	-----	---	-----	---	--/--/-- /-----
2) -----	-----	---	-----	---	--/--/-- /-----

G. QUALIFIED CENTRE FOR COLLECTION OF MICRO-ORGANISM CULTURES,
NAME-----

H. SPECIAL REMARKS

DOCUMENTATION ATTACHED

RESERVATIONS PUT ASIDE

	NR. ITEMS	DATE	FILE NR.
DOC 1)	2 PROV NR. PAGES 25 ABSTRACT WITH MAIN DRAWING, DESCRIPTION AND CLAIMS (1 COPY IS MANDATORY)	--/--/-- /	-----
DOC 2)	0 PROV NR. PAGES 00 DRAWING (MANDATORY IF CITED IN THE DESCRIPTION, 1 COPY)	--/--/-- /	-----
DOC 3)	0 RES. POWER OF ATTORNEY ILLEGIBLE	--/--/-- /	-----
DOC 4)	0 RES. DESIGNATION INVENTOR	--/--/-- /	-----
DOC 5)	0 RES. PRIORITY DOCUMENT WITH ITALIAN TRANSLATION	--/--/-- /	-----
DOC 6)	0 RES. AUTHORIZATION OR ASSIGNMENT DEED	--/--/-- /	-----
DOC 7)	0 RES. COMPLETE NAME OF THE APPLICANT	--/--/-- /	-----

8) PAYMENT CONFIRMATION, TOTAL LIRE fivehundred and sixtyfive=

FILLED ON 14/04/2000

SIGNATURE OF THE APPLICANT (S)

Avv. RAPISARDI MARIACRISTINA

MORE PAGES YES/NO NO

UFFICIO BREVETTI RAPISARDI S.r.l.

A CERTIFIED COPY OF THE PRESENT DEED IS REQUIRED YES/NO YES

PROVINCE OFFICE INDUSTRY, COMMERCE AND HANDYCRAFT OF MILAN

RECORD OF FILING APPLICATION NUMBER MI2000 A 000850

On year onethousand TWO THOUSAND day FOURTEEN of month APRIL

the applicant(s) has (have) filed before the undersigned the present application
along with -- additional sheet for the granting of the above mentioned patent

ANY REMARK BY THE OFFICER

Impressed circular stamp

THE APPLICANT

THE OFFICER

ABSTRACT OF THE INVENTION WITH MAIN DRAWING, DESCRIPTION
AND CLAIM

APPLICATION NUMBER MI2000A 000850 FILING DATE 14/04/2000

PATENT NUMBER DATE OF GRANT --/--/----

B. TITLE

PROCESS FOR MAKING A FOAMED THERMOPLASTIC ELASTOMERIC MATERIAL, IN
PARTICULAR FOR MAKING CORKS OR CLOSURES FOR CONTAINERS IN
SUBSTITUTION OF NATURAL CORK, MATERIAL OBTAINED THROUGH THIS
PROCESS AND CLOSURES MADE OF THIS MATERIAL

I. ABSTRACT

A process for making a foamed thermoplastic elastomeric material,
in particular for making corks or closures for containers in
substitution of natural cork, in which process the preparation is
foreseen of a first component formed of a thermoplastic
elastomeric compound, and a second component, formed of a
thermoplastic elastomeric compound which contains at least one
foaming agent, the mixing of said first and second components and
the moulding of this mixture.

The thermoplastic material obtained with this process offers the
advantage of permitting the making of closures in general, and in
particular corks for wine bottles or demijohns or for bottles for
distillates and liquors, which has aesthetic and functional
characteristics which are equal to or greater than those of
analogous corks in natural cork.

DRAWING

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The present invention concerns a new foamed thermoplastic elastomeric material, particularly adapted for making corks or closures of containers, for example for drinks and foods, in substitution of natural cork.

Natural cork was and still is commonly used for making considerably quantities of corks and in general closures for bottles and containers typically for liquids, and particularly in the wine sector and in the alcoholic drink and distillate sector.

The set of these factors makes the production and use of natural-cork corks more costly each year, and has lead bottlers to evaluate the possibility of using alternative synthetic materials for making corks, thus overcoming a traditional mistrust towards such products.

Nevertheless, in order to ensure a favourable reception, not so much by the bottler as by the final consumer, the synthetic cork must maintain aesthetic and “feeling” characteristics which are analogous to those of the natural cork, along with of course the imperative functional characteristics of sealing, ease of uncorking with traditional instruments (corkscrews), ease of use, absence of contamination of the bottled product, absence of odour.

The use of synthetic corks made, for example, in polyethylene or metal screw corks equipped with inner seal is known to all. Nevertheless the sector of wine producers or distillate producers is very much against the use of such closures, which remain limited to economical products or those of low quality.

The consumers themselves, faced with a bottle of wine or grappa closed with polyethylene cork or metal screw corks, commonly perceive to be in front of a low quality product – independent from the real contents of the bottle itself.

The main object of the present invention is that of providing a process for making a new foamed thermoplastic material, particularly adapted to manufacturing corks or closures of containers for drinks and foods in general, in substitution of the natural cork.

The invention moreover has the object of providing a preparation process of said foamed thermoplastic material, so to make the latter easily adapted to moulding processes which are even different from each other, both due to the conformation of the employed moulding machine (rotating or static) and for the type of mould or design of the manufactured item to be made.

A further object of the present invention consists of providing a foamed thermoplastic material adapted for permitting the making of corks having aesthetic and functional characteristics which are equal to or greater than those of analogous corks in natural cork.

These and other objects are achieved with the process and with the thermoplastic material of the independent claims, respectively 1 and 19.

Further characteristics regarding this material, the mentioned process and the corks and closures made with it are evident in the remaining claims.

The thermoplastic material according to the invention offers the advantage of permitting the making of closures in general, and in particular corks for bottles or demijohns of wine, or bottles of distillates and liquors, which have aesthetic and functional characteristics which are equal to or greater than analogous corks in natural cork.

Further characteristics, objects and advantages will be clear from the following description of the plastic material and the process of the present invention, undertaken with reference also to the examples which will be illustrated below.

In the present invention, during the design, the following requirements were considered which the material must have and/or must be able to confer to the final manufactured item:

- can be injection moulded
- possibility of adapting the material to different processes and/or moulding systems
- suitability for contact with foods or for medical use of the employed raw materials
- surface finishing of the manufactured item similar to that of natural cork
- sufficient elasticity, so to ensure the closure seal
- sufficient resistance to tearing so to ensure an easy uncorking by means of corkscrews
- weight analogous to that of natural cork
- resistance to water, to bases, acids and alcohol
- sufficient resistance to temperature and ozone in order to ensure an adequate lifetime of the closure
- substantial absence of oxygen absorption
- absence of odour or taste

As a function of the above-listed requirements, the raw materials held to be most suited were chosen to make the material of the invention.

In particular, the following raw materials were taken into consideration, subdivided by category:

Thermoplastic pure elastomers (TPE)

- Styrene-Ethylene / Butylene-Styrene (SEBS) Copolymers: for example Kraton G® produced by Shell or Septon® produced by Kuraray.
- Styrene-Ethylene / Propylene-Styrene (SEPS) Copolymers: for example Kraton G® produced by Shell or Septon® produced by Kuraray.

- Styrene (Ethylene-Ethylene / Propylene)-Styrene (SEEPS) Copolymers: for example Kraton Septon® produced by Kuraray.
- Styrene-Butadiene-Styrene (SBS) Copolymers: for example Kraton D® produced by Shell or Europrene SOL T® produced by EniChem.

Plastomers

- Polypropylene homopolymer (PPhomo): for example Moplen® produced by Montell or Daplen® produced by Borealis.
- Polypropylene copolymer (PPcopo): for example Moplen® and Adflex® produced by Montell or Daplen® produced by Borealis.
- Polyethylene-vinyl acetate (EVA): for example Greenflex® produced by Polimeri Europa or Escorene UL® produced by Polimeri Europa or Escorene LD® produced by Exxon Chemical.
- Low-density polyethylene (LDPE): for example Riblene® produced by Polimeri Europa or Escorene LD® produced by Exxon Chemical.

Plasticisers

- Paraffin-base mineral oil (medical grade): for example Primol® or Marcol® produced by Esso or Agip OBI® produced by Agip Petroli

Mineral fillers

- Calcium carbonate (CaCO₃)

Foaming agents

- Azodicarbonic acid diamide or Azodicarbonamide (AZDC) both pure and modified: for example Profor® and Genitron® produced by Bayer.
- Endothermic foaming agents such as mixtures of sodium bicarbonate and citric acid: for example Hydrocerol® and Exocerol® produced by Clariant.

Other additives

- Oleoamide: for example Crodamide® produced by Croda Universal.

- Erucamide: for example Crodamide® produced by Croda Universal.
- Calcium stearate

In the making of the material, object of the present invention, an important parameter to be considered is the hardness, measured according to the Shore A scale in accordance with the regulations ISO 868, UNI 4916, DIN 53505, ASTM D 2240, etc.

In general, the hardness range which resulted suitable is in the range of 60-95 Shore A. In particular, it is possible to identify two specific ranges as a function of the final application:

- a. 60-85 Shore A for corks of distillate and liquor bottles
- b. 80-90 Shore A for corks of wine bottles and for demijohns or casks.

A second aspect to take into account is the correlation between the final expansion efficiency of the foaming agent and the process temperature used both for the production of the thermoplastic material and for the transformation of this material into the final manufactured item. In fact, the action mechanism of the foaming agents is based on the emission of gases deriving from the thermal decomposition of the foaming agent activated by the temperature.

The typical activation temperature of the decomposition process varies from foaming agent to foaming agent, and for the products chosen in achieving the present invention is in the range of 140°C – 230°C.

This temperature range is also typical for the production of the raw material mixture by means of an extrusion process.

The overlapping of the foaming agent decomposition temperature with the temperature for making the materials renders ineffective and counter-productive the introduction of the foaming agent directly into the starting material, since this would activate its decomposition in the extruder cylinder and not afterward, during the injection moulding process.

The expansion being activated by the temperature, this is in some manner “lost” each time the foaming agent undergoes a thermal process, and its effect tends to rapidly diminish with every subsequent thermal cycle.

All of the above provides one of the two reasons for which it was decided to introduce the foaming agent immediately before the injection moulding process.

The second reason is tied to the flexibility of the “material system”, since different technologies of moulding have been observed which require different doses of foaming agent to obtain the same result.

Making of the elastomeric component (first component)

Examples 1A - 1P

The objective is that of making a thermoplastic elastomeric compound which has the desired characteristics.

With these first examples, it is desired to evaluate the possible formulation solutions.

In Table I, the type formulations are visible with final hardness in the range of 80-90 Shore A. The quantities are indicated in phr (Parthundred rubber).

Table 1

Component	1.A	1.B	1.C	1.D	1.E	1.F	1.G	1.H	1.I	1.J	1.K	1.L	1.M	1.N	1.O	1.P
HMW SEBS (1)	100				100				100				100			
MMW SEBS (2)		100				100				100				100		
HMW SEEPS (3)			100				100				100				100	
MMW SEEPS (4)				100				100				100				100
Plasticiser Oil (5)	80	50	80	50	80	50	80	50	80	50	80	50	80	50	80	50
PP homo MFI=6 (6)	80	80	80	80												
PP homo MFI=30+40 (7)					80	80	80	80								
PPcopo MFI=8 (8)									450	450	450	450				
EVA MFI=2VA=18% (9)													450	450	450	450

Examples 2A – 2P

Analogously, in Table 2 a second series of type formulations is visible, having final hardness in the range of 65-80 Shore A. The quantities are in phr.

Table 2

Component	2.A	2.B	2.C	2.D	2.E	2.F	2.G	2.H	2.I	2.J	2.K	2.L	2.M	2.N	2.O	2.P
HMW SEBS (1)	100				100				100				100			
MMW SEBS (2)		100				100				100				100		
HMW SEEPS (3)			100				100				100				100	
MMW SEEPS (4)				100				100				100				100
Plasticiser Oil (5)	80	50	80	50	80	50	80	50	80	50	80	50	80	50	80	50
PP _{homo} MFI=6 (6)	40	40	40	40												
PP _{homo} MFI=30+40 (7)					40	40	40	40								
PP _{copo} MFI=8 (8)									250	250	250	250				
EVA MFI=2VA=18% (9)													250	250	250	250

(1) Shell Kraton G 1651 – HMW=High Molecular Weight

(2) Shell Kraton G 1650 – MMW=Medium Molecular Weight

(3) Kuraray Septon 4055 – HMW=High Molecular Weight

(4) Kuraray Septon 4033 – MMW=Medium Molecular Weight

(5) Esso Primoil 352

(6) Montell Moplen C 30 G

(7) Montell Moplen H 32 GA or Borealis Daplen RS 103

(8) Montell Adflex x 100 G

(9) Polimeri Europe Greenflex ML50 or Exxon Escorene Ultra UL00218

The thermoplastic elastomeric component (first component) can be made on two twin-screw extruders, a co-rotating Maris TM 30 MP equipped with water-cooled cutter at the head, or a counter-rotating Bausano MD2 30/19 equipped with cord cutter.

On both extruders, working temperatures were in the range of 160-210°C.

Examples 3A – 3P and 4A – 4P

On the basis of the results obtained in the preceding examples, the following formulation choices were made, from which the formulations of Tables 3 and 4 follow (quantities in phr):

a. Elastomeric part: use of a mixture with 50/50 HMW/MMW elastomer ratio, both of SEBS and SEEPS type. This choice permits optimising the fluidity of the product in the injection moulding step.

b. Plastomeric part:

b.1 use of the PP copolymer, Adflex X100g type, produced by Montell,

b.2 use of a mixture with ratio variable from 34/66 – 15/85 of PPhomo MFI=6 (Moplen C30G Type)/EVA

b.3 use of a mixture with ratio variable from 34/66 – 15/85 of PPhomo MFI=6 (Moplen C30G Type)/PPcopo (Adflex X100G type).

During the final definition, the opportunity was moreover evaluated for using both mineral fillers and possible sliding agents.

Table 3

Component	3.A	3.B	3.C	3.D	3E	3.F	3.G	3.H	3.I	3.J	3.K	3.L	3.M	3.N	3.O	3.P
HMW SEBS (1)	50	50	50	50	50						50		50		50	
MMW SEBA (2)	50	50	50	50	50						50		50		50	
HMW SEEPS (3)						50	50	50	50	50	50		50		50	
MMW SEEPS (4)						50	50	50	50	50	50		50		50	
Plasticiser Oil (5)	50	50	50	50	50	50	50	50	50	50	50	50	50	50	50	50
PPhomo MFI=6 (6)		60	40	60	40		60	40	60	40			40	40	40	40
PPcopo MFI=8 (8)	450			115	230	450			115	230	450	450			230	230
EVA MFI=2VA=18% (9)		115	230				115	230					230	230		

Table 4

Component	4.A	4.B	4.C	4.D	4E	4.F	4.G	4.H	4.I	4.J	4.K	4.L	4.M	4.N	4.O	4.P
HMW SEBS (1)	50	50	50	50	50						50		50		50	
MMW SEBA (2)	50	50	50	50	50						50		50		50	
HMW SEEPS (3)						50	50	50	50	50	50		50		50	
MMW SEEPS (4)						50	50	50	50	50	50		50		50	

Table 6

Characteristics	4.A	4.B	4.C	4.D	4.E	4.F	4.G	4.H	4.I	4.J	4.K	4.L	4.M	4.N	4.O	4.P
Hardness	68	71	70	72	70	70	75	72	74	73	70	69	72	71	72	72
Shore A (1)																
Melt Flow	19.6	17.9	17.1	18.7	19.3	17.2	16.6	15.8	16.9	17.1	18.0	18.6	16.7	16.0	18.0	18.2
Index-g/10' (2)																
Density at 23°C	0.87	0.89	0.90	0.88	0.88	0.87	0.90	0.90	0.89	0.89	0.87	0.87	0.90	0.90	0.88	0.88
g/cm ² (3)																
Ultimate load	7.6	7.0	6.8	8.8	8.6	8.2	7.4	7.0	9.1	8.8	8.0	7.9	7.0	6.9	8.7	8.5
Mpa																
Ultimate	815	841	869	802	790	810	832	855	795	775	806	811	848	860	800	790
elongation = % (4)																

(1) after 3 sec-3 overlapping 2mm plates (ref. ISO 868, ASTM D 2240, DIN 53505, UNI 4916)

(2) at 190° with 5 Kg (ref. ISO 1133, ASTM D 1238, DIN ISO 1133, UNI 5640)

(3) determined on non-foamed material (ref. ISO 1183, ASTM D 792, DIN 53479, UNI 7092)

(4) test piece DIN 52, 50 mm/min (ref. DIN 53504, ISO 37, ISO 527)

It is observed from the obtained data that the differences following the use of SEBS rather than SEEPS are in fact irrelevant with respect to the final functionality, both regarding the hardness and fluidity; therefore, from now on, SEBS/SEEPS will be referred to as practically interchangeable products with regard to the present invention.

Moreover, the examples of the tables 3 and 4, while showing improved characteristics of expansion homogeneity with respect to the examples of tables 1 and 2, with a lower quantity of PPhomo are foamed in a more homogeneous manner than those with a higher quantity of PPhomo.

The introduction of several compounds of a mineral filler (CaCO₃) has modified the mechanical characteristics of the material, leading to a reduction of the tensile properties (ultimate load and elongation).

Making the elastomeric component with high foaming agent content (second component)

The objective is to make a compound with high concentration of foaming agent, without this being “lost” during the preparation process of the same.

As carrier, two formulations were chosen based on components which permit the working in a twin-screw extruder at temperatures lower than 140°C (see Table 7).

Table 7

[illegible]

<i>Foaming agent</i>				
AZDC (POROFOR ADC/L-C2)	30	30	40	40
Modified AZDC (GENITRON EPA)	30	30	40	40
Endothermic agent (HYDROCEROL BIH)	30	30	40	40

(1) Shell Kraton D 1186 or EniChem Europrene SOL T 161/8

(2) Polimeri Europa Riblene MV10

(3) Polimeri Europa Greenflex ML50 or Exxon Escorene Ultra UL 00218

(4) Esso Primoil 352

The foaming compounds can be made on two twin-screw extruders, a co-rotating Maris TM 30 MP equipped with water-cooled cutter at the head, or a counter-rotating Bausano MD2 30/19 equipped with cord cutter. On both extruders, it is possible to obtain the compounds of Table 7 at temperatures lower than 130°C and without appreciable foaming agent losses.

Nevertheless, several critical productive instability states were observed in making the foaming compounds with the 40% Genitron EPA (7.H and 7.K) and with the 40% Hydrocerol (7.I and 7.L) which lead one to prefer the 30% foaming agent formulations from a production standpoint.

Making the thermoplastic material of the present invention

Based on the results reported in the preceding tables, preferred formulations were prepared both for the first component (examples 8.A – 8.H, Table 8) and for the second component (examples 9A – 9H, Table 9), adapted for preparing the thermoplastic material of the invention.

In these tables, the parts are expressed in phr.

Table 8 (first component)

	Hardness from 80-90 Shore A			Hardness from 65-80 Shore A			85 Shore A	70 Shore A
	8A	8B	8C	8D	8E	8F	8G	8H
Component								

HMW SEBS/SEEPS (1)	50	50	50	50	50	50	50	50
MMW SEBS/SEEPS (2)	50	50	50	50	50	50	50	50
Plasticiser oil (3)	50	50	50	60	60	60	50	60
PPcopo MFI=8 (4)	400-500		100-250	200-300		50-120	450	250
PPhomo MFI=6 (5)		30-70	30-70		15-35	15-35		
EVA MFI=2VA=18% (6)		100-250			50-120			
CaCO ₃	0-100	0-100	0-100	0-100	0-100	0-100		

(1) Shell Kraton G 1631 or Kuraray Septon 4055

(2) Shell Kraton G 1650 or Kuraray Septon 4033

(3) Esso Primoil 352

(4) Montell Adflex X 100 G

(5) Montell Moplen C 30 G

(6) Polimeri Europa Greenflex ML 30 or Exxon Escorene Ultra UL 00218

Table 9 (second component)

<i>Components of the Carrier</i>	9A	9B	9C	9D	9E	9F	9G
dry HMW SBS (1)	100	100	100	100	100	100	100
Plasticiser oil (2)	100	100	100	100	100	100	100
LDPE MFI=65 (3)	150-300	150-300	150-300				
EVA MFI=2 VA=18% (3)				150-300	150-300	150-300	
<i>Foaming agent</i>							
AZDC (PROROFOR ADC/L=C)	200-300			200-300			
Modified AZDC (GENITRON EPA		160-280			160-280		200
Endothermic foaming agent			160-280			160-280	

(HYDROCEROL BIB)							
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(1) Shell Kraton S 1186 or Enichem Europrene SOL L 161/b

(2) Esso Primoil 352

(3) Polimeri Europa Riblene MV10

(4) Polimeri Europa Greenflex ML50 or Exxon Escorene Ultra UL 00218

For the making of corks of bottles or containers in general, a mixture formed by 97% by weight of the first component of the example 8G and 3% by weight of the second component of the example 9G was shown to be particularly advantageous.

This mixture was found to be particularly suited for the injection moulding of wine bottle corks, with the use of static injection moulding machines, with temperatures in the range of 180-200°C.

An optimal configuration for making the same manufactured item, though on a rotating injection press with temperatures which range from 190-210°C, is the following:

First component, ex. 8G: 98.0% by weight

Second component, ex. 9G: 2.0% by weight

The foaming component type 9G can be inserted in the mixture of the material of the invention up to a maximum of 6.5% by weight. Beyond this limit, the maximum quantity of AZDZ allowed by current international law for the suitability of contact with foods is exceeded.

In any case, compositions are equally effective with 96-99% of the first component and 1-4% of the second component.

For foaming components with AZDC quantities other than 200 phr, it will be necessary each time to determine the maximum limit admitted based on the AZDZ amount inserted into the foaming component. In the case of use of endothermic foaming agents (for example Hydrocerol produced by Clariant), these compounds being mixtures of citric acid sodium bicarbonate, they are not subjected to particular limitations.

CLAIMS

1. Process for making a foamed thermoplastic elastomeric material, in particular for making corks or closures for containers in substitution of natural cork, characterised in that it foresees the preparation of a first component, formed by a thermoplastic elastomeric component, and a second component, formed by a thermoplastic elastomeric component which contains at least one foaming agent, the mixing of said first and second components and the moulding of this mixture.
2. Process according to claim 1, characterised in that said first component is formed by mixing one or more thermoplastic elastomeric compounds with one or more plastomers and with one plasticiser.
3. Process according to claim 1, characterised in that said second component is formed by mixing a thermoplastic elastomeric component with a plastomer, with a plasticiser and with a foaming agent.
4. Process according to claim 3, characterised in that said mixture is made at a lower temperature than that of activation of the mentioned foaming agent.
5. Process according to claims 3 and 4, characterised in that said plastomer has a low melting point.
6. Process according to claim 5, characterised in that said plastomer has a melting point less than 140°C.
7. Process according to claim 6, characterised in that said temperature is in the range of 85-108°C.
8. Process according to one or more of the claims 3-7, characterised in that said foaming agent is chosen from:
 - Azodicarbonic acid diamide or Azodicarbonamide (AZDC), pure or modified.
 - Endothermic foaming agents such as mixtures of sodium bicarbonate and citric acid.

9. Process according to one or more of the preceding claims, characterised in that said thermoplastic elastomeric compounds are chosen from:
- Styrene-Ethylene / Butylene-Styrene (SEBS) Copolymers
 - Styrene-Ethylene / Propylene-Styrene (SEPS) Copolymers
 - Styrene (Ethylene-Ethylene / Propylene)-Styrene (SEEPS) Copolymers
 - Styrene-Butadiene-Styrene (SBS) Copolymers
10. Process according to one or more of the preceding claims, characterised in that said plastomers are chosen in the group formed by:
- Polypropylene homopolymer (PPhomo)
 - Polypropylene copolymer (PPcopo)
 - Polyethylene-vinyl acetate (EVA)
 - Low density polythethylene (LDPE)
11. Process according to one or more of the claims 3-10, characterised in that said plastomer is composed either of an ethylene-vinyl acetate copolymer (EVA) with VA content equal to about 18% and with melting point in the range of 85-90°C, or of a low density polyethylene (LDPE), with melting point in the range of 103-108°C, or of the mixture of both.
12. Process according to one or more of the preceding claims, characterised in that said plasticiser is a paraffin-base mineral oil.
13. Process according to claim 2, characterised in that a mineral filler is added to the mixture of said first component.
14. Process according to claim 13, characterised in that said mineral filler is composed of calcium carbonate.
15. Process according to claim 2, characterised in that said mixture of the mentioned first component is prepared at a temperature in the range of 160-210°C.

16. Process according to one or more of the preceding claims, characterised in that the injection moulding of the mixture of said first and second components is carried out at a temperature in the range of 180-210°C.
17. Process according to claim 16, characterised in that said moulding is of static injection type, carried out at the temperature of $180 \div 200^{\circ}\text{C}$.
18. Process according to claim 16, characterised in that said moulding is of rotating injection type, carried out at the temperature of $190 \div 210^{\circ}\text{C}$.
19. Foamed thermoplastic elastomeric material, particularly for making corks or closures for containers in substitution of natural cork, obtained with the process according to one or more of the preceding claims, characterised in that it comprises a first component, formed by a thermoplastic elastomeric compound, and a second component, composed of a thermoplastic elastomeric compound which contains at least one foaming agent.
20. Material according to claim 19, characterised in that said first component is formed by mixing one or more thermoplastic elastomeric compounds, with one or more plastomers and with a plasticiser.
21. Material according to claim 19, characterised in that said second component is formed by the mixture of a thermoplastic elastomeric compound with a plastomer, with a plasticiser and with a foaming agent.
22. Material according to the preceding claim, characterised in that said plastomer is a plastomer with low melting point.
23. Material according to claim 22, characterised in that said plastomer has a melting point lower than 140°C .
24. Material according to one or more of the preceding claims, characterised in that said thermoplastic elastomeric compounds are chosen from:
 - Styrene-Ethylene / Butylene-Styrene (SEBS) Copolymers
 - Styrene-Ethylene / Propylene-Styrene (SEPS) Copolymers

- Styrene (Ethylene-Ethylene / Propylene)-Styrene (SEEPS) Copolymers
- Styrene-Butadiene-Styrene (SBS) Copolymers

25. Material according to one or more of the preceding claims, characterised in that said plastomers are chosen in the group formed by:

- Polypropylene homopolymer (PPhomo)
- Polypropylene copolymer (PPcopo)
- Polyethylene-vinyl acetate (EVA)
- Low density polythethylene (LDPE)

26. Material according to claim 21, characterised in that said plastomer is composed of a ethylene-vinyl acetate (EVA) copolymer with VA content equal to about 18% and with melting point in the range of 85-90°C, and a low density polyethylene (LDPE) with melting point in the range of 103-108°C.

27. Material according to one or more of the preceding claims, characterised in that said plasticiser is a paraffin-base mineral oil.

28. Material according to claim 21, characterised in that said foaming agent is chosen from:

- Azodicarbonic acid diamide or Azodicarbonamide (AZDC), pure or modified.
- Endothermic foaming agents such as mixtures of sodium bicarbonate and citric acid.

29. Material according to claim 20, characterised in that a mineral filler is added to the mixture of said first component.

30. Material according to any one of the preceding claims, characterised in that it comprises:

96-99% by weight of said first component, composed of:

- a thermoplastic elastomeric compound formed by a mixture containing 50 phr of HMW SEBS or SEEPS and 50 phr of MMW SEBS or SEEPS;
- 50-60 phr of a plasticiser oil; and
- 50-500 phr of PPcopo with MFI equal to 8;

and of 1-4% by weight of said second component, composed of:

- 100 phr of dry HMW SBS;
- 100 phr of plasticiser oil;
- 150-300 phr of LDPE with MFI equal to 65; and
- 150-300 phr of modified AZDC, or Hydrocerol type endothermic foaming agent.

31. Material according to one or more of the preceding claims, characterised in that it has a hardness in the range of 60-95 Shore A.

32. Closure for containers, characterised in that it is made with the material according to one or more of the preceding claims in substitution of natural cork.

33. Closure according to claim 32, characterised in that it is a cork.

34. Closure according to one or more of the preceding claims for use as a cork for bottles of distillates and liquors, characterised in that said material has a hardness in the range of 65-80 Shore A.

35. Closure according to one or more of the preceding claims for use as a cork for wine bottles and for demijohns or casks, characterised in that said material has a hardness in the range of 80-90 Shore A.

All as substantially described, illustrated and for the objects herein specified.

Milan,